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PYRAZOLE DERIVATIVES AS POLYETHYLENE OXIDATIVE DESTRUCTION STABILIZERS

The possibility of newly synthesized pyrazole derivatives using as heat stabilizers of high-pressure polyethylene (LDPE): 1-acetyl-4-methyl-3(5)-(2-(3-nitrophenyl)vinyl)-1*H*-pyrazole (additive 1) and 4-benzoyl-3-(2-(4-nitrophenyl)vinyl-5-phenyl-1-tosyl-1*H*-pyrazole (additive 2)) has been studied. It is established that the introduction of additive 1 or 2 in the amount of 0,05-0,10 wt % to the high-pressure polyethylene leads to the increasing of such physical-mechanical properties of the samples as tensile strength by 1,2–1,5 times and elongation by 2,3–3,0 times in comparison with the unstabilized sample. Synthesized substances are more effective than Tioalkofen MBP used in industry.

Introduction. Thermal effects on polymers, particularly polyethylene (LDPE), facilitates their rapid expansion, which, in turn, negatively affects the physical and mechanical properties of polymeric materials and significantly reduces the life cycle of their products.

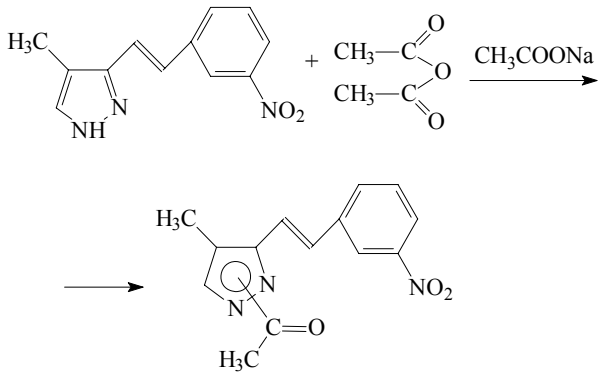
The aging of polymers may be inhibited by introducing the required amount of special chemicals – stabilizers. These additives significantly increase the stability of the materials, their resistance to external influences, extend the application range of polymer products and prolong their service life.

It is obvious that with the increasing of service life of polymer products, material and energy costs are significantly reduced both at the stage of obtaining the latter and waste recycling.

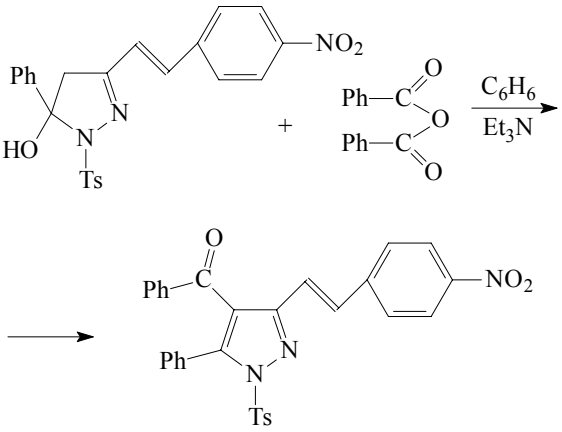
Main part. This paper investigates the possibility of using new pyrazole derivatives which were first synthesized at the Department of Organic Chemistry, EI "BSTU" [1, 2] as stabilizers of high-pressure polyethylene oxidative degradation.

1-acetyl-4-methyl-3(5)-(2-(3-nitrophenyl)-vinyl)-1H-pyrazole (additive 1), and 4-benzoyl-3-(2-(4-nitrophenyl)vinyl)-5-phenyl-1-tosyl-1H-pyrazole (additive 2) have been used as the additives.

Additive 1 was obtained by acetylation of 4-methyl-3-(2-(3-nitrophenyl)vinyl)-1H-pyrazole with acetic anhydride with 92% yield:



Additive 2 was obtained by reaction of benzoic anhydride and 5-hydroxy-3-(2-(4-nitrophenyl)vinyl)-5-phenyl-1-tosyl-4,5-dihydro-pyrazole with 81% yield:



The structures of the compounds were proved by using of modern physical (IR and NMR spectroscopy) and chemical methods. These spectra are shown in the experimental section. Thus, in the IR spectrum of additive 2 the characteristic absorption band of the hydroxyl group of the initial synthon is absent, and the absorption band at 1648 cm^{-1} is observed, which indicates the presence of the carbonyl group conjugated with an aromatic ring [3]. The absorption bands of asymmetric and symmetric stretching vibrations of the S=O group in tosyl fragment appear at 1394 and 1170 cm^{-1}, respectively. In the ^1H NMR spectra of the compound AB-spin system of the signals of pyrazole cycle methylene protons in the initial substrates disappears. This indicates that dehydration occurred.

Testing of stabilizing properties of additives was conducted according to the following method: linkage of polyethylene mass of 30 g was placed on the heated laboratory mikrorollers (temperature of the hot roll 140°C), and under vigorous stirring the specified amount of heat stabilizer (0.05, 0.1,

and 0.2 wt %) was added to obtain homogenized mass. Within 1–2 minutes the films were pressed on a heated press at t = 160–180°C and pressure of 3.2 kg/cm^2, than they were cut into equal strips. The latter were placed in a thermal cabinet, where they were heated to 90°C for 24, 48 and 72 h.

Since the products of LDPE are used mainly in an environment characterized by tensile force, then it is appropriate to study the effect of additives on elasticity and tensile strength. The deformation and strength characteristics of the material were determined by a tensile testing machine RMI-60 according to the State Standard 11262-80 at (20 ± 2)°C and the cargo weight of 30 kg.

Tear strength is determined according to the following formula:

$$\sigma = F / S,$$

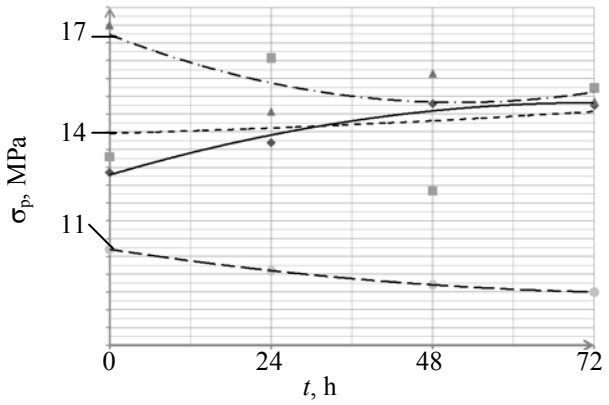
where σ – tear strength, F – intension, H; S – cross-sectional area of the polymer sample, mm^2.

The area is determined by the following formula:

$$S = h \cdot \delta,$$

where h – width of the working area of the sample, mm, in all experiments h = 10 mm; δ – sample thickness, mm.

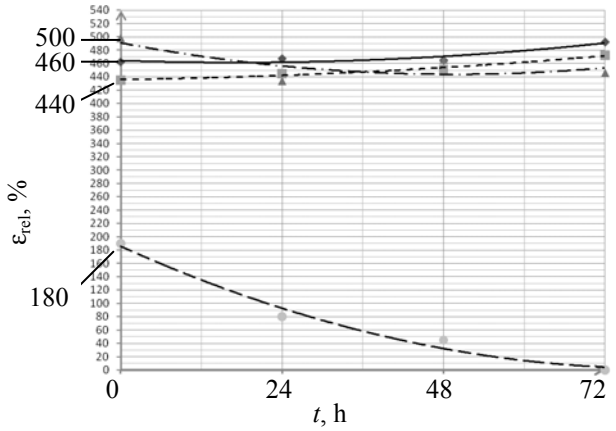
Experimental data (change of tensile strength (MPa) and elongation (%) of polymer samples from the aging time and the content of stabilizers 1 and 2 are shown in Fig. 1–4.



– – without a stabilizer — 0.05%; --- 0.1%; – - – 0.2%

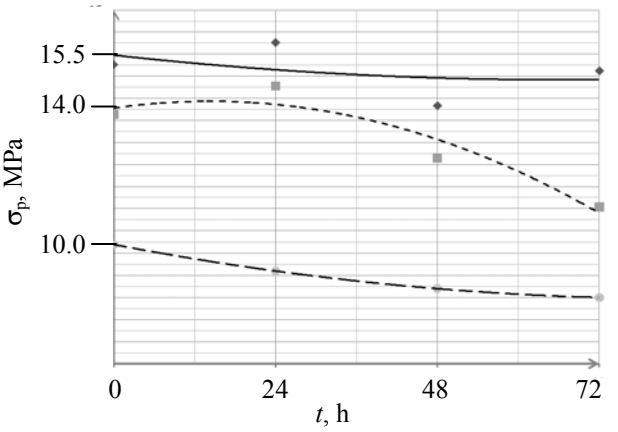
Fig. 1. Change in tensile strength of polymer samples (σ_p, MPa) depending on the time of aging and the percentage of additive 1

Analysis of the dependence (Fig. 1) suggests that the introduction of additive 1 increases the tensile strength of the test samples in comparison with non-stabilized polyethylene. In the aging process of modified samples their strength is increased (when the content of the stabilizer is 0.05–0.10 wt %). There is a point of view according to which the additive molecules can trap energy from the outside [4]. This theory can be applied to the studied substances in view of their structures in extended systems of conjugated bonds. We can also assume that the molecules of additives not only inhibit oxidative degradation of LDPE, but also facilitate cross-linking of the polymer macromolecules, which increases its strength.



– – without a stabilizer ; — 0.05%; --- 0.1%; – - – 0.2%

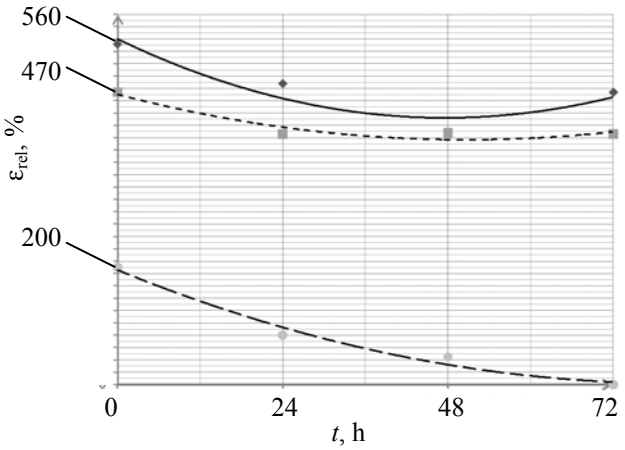
Fig. 2. Change in elongation (ε,%) of polymer samples depending on the time of aging and the percentage of additive 1



– – without a stabilizer; — 0.05%; --- 0.1%

Fig. 3. Change in tensile strength of polymer samples (σ_p, MPa) depending on the time of aging and the percentage of additive 2

According to Fig. 3 and 4, the compositions containing a stabilizer 2 (0.05%) exhibit good mechanical properties throughout the period of aging. For compositions containing stabilizer 0.1% after 72 h of aging strength deteriorates, but it is higher in comparison with the strength of non-aging samples. The elasticity of the samples is somewhat reduced after 72 h of aging, but only slightly (Fig. 4). This can be explained mainly by the occurrence of the cross-linking during aging, rather than destruction of these samples.



– – without a stabilizer; — 0.05%; --- 0,1%

Fig. 4. Change in elongation of polymer samples (ε, %) depending on the time of aging and the percentage of additive 2

In general, all compositions exhibit good mechanical properties up to 48 hours of aging. With increasing duration of heat exposure to 72 h strength of samples is reduced. Flexibility remains practically at the initial level without significant oscillations (Fig. 2 and 4). Thus, the best physical and mechanical properties were observed in samples of polymer stabilized by additive 1 in quantities of 0.05–0.20 wt. %. The introduction of 1-acetyl-4-methyl-3(5)-(2-(3-nitrophenyl)vinyl)-1H-pyrazole (stabilizer 1) remains flexible without any change in comparison with the original polyethylene with aging up to 72 hours inclusive, while maintaining high strength at break.

The effectiveness of the other stabilizer (4-benzoyl-(3-(2-(4-nitrophenyl)vinyl)-5-1-tosyl-phenyl-1H-pyrazole) is slightly lower, but the values of ε and σ_p are higher than the compositions using commercially used stabilizers (for example, when the content of photostabilizer tinuvin in the samples of high-density polyethylene is 0.8 wt. %, aging factor for tensile strength is equal to 0.74) [5]. Aging factors in strength of the investigated samples are determined by the formula:

$$K_{st} = \sigma \text{ (after aging)} / \sigma \text{ (before aging)}$$

Aging factor for strength of LDPE samples stabilized with additives 1–2 when their concentration is 0.1%

Additive	Time of aging, h		
	24	48	72
1-Acetyl-4-methyl-3(5)-(2-(3-nitrophenyl)vinyl)-1H-pyrazole (stabilizer 1)	1.2	0.93	1.15
4-Benzoyl-3-(2-(4-nitrophenyl)vinyl-5-phenyl-1-tosyl-1*H*-pyrazole (stabilizer 2)	1.05	0.93	0.84

Experimental part. The IR spectra of the compounds were recorded on a FT-IR spectrometer «Nexus» («Nicolet») in tablets of KBr. NMR spectra of synthesized substances in $CDCl_3$ solutions with TMS as internal standard were obtained using the spectrometer «Bruker AVANCE» (400 MHz). Monitoring the progress of the reaction was carried out by TLC on silica gel plates "Kieselgel 60 F_{254}" (Merck), eluting agent – ether-petroleum ether.

Cleaning solvents was determined by standard methods [6].

1-Acetyl-4-methyl-3(5)-(2-(3-nitrophenyl)-vinyl)-1H-pyrazole (additive 1).

Freshly prepared acetic anhydride (3.0 mL) and anhydrous sodium acetate (0.1 g) are added to 4-methyl-3-(2-(3-nitrophenyl)vinyl)-1H-pyrazole (1.0 mmol). All substances are dissolved by mild heating (up to 50°C) and leaved for 15–25 hours without heating. Then reaction mixture diluted twice with water and after 1h neutralized with 10% solution of NaOH, the precipitate is filtered off and washed with water. The yield makes up 92%. Mp. = 180–182°C.

IR-spectrum (ν, cm^{-1}): 1731 (C=O), 1525 (NO_2), 1350 (NO_2).

NMR-spectrum (ppm., *J* Hz): 2.13 (3H, d, $J = 0.5$, 4-CH_3-het.), 2.52 (3H, d, $J = 0.5$, 5-CH_3-het.), 2.72 (3H, s, CH_3-C=O), 7.14 (1H, d, $J = 16{,}4$, CH=), 7.41 (1H, d, $J = 16.4$, HC=), 7.54 (1H, m, C_6H_4), 7.82 (1H, m, C_6H_4), 8.13 (1H, m, C_6H_4), 8.39 (1H, m, C_6H_4).

4-Benzoyl-3-(2-(4-nitrophenyl)vinyl)-5-phenyl-1-tosyl-1*H*-pyrazole (additive 2).

0.226 g (1.0 mmol) of freshly prepared benzoic anhydride is dissolved in 10 ml of benzene. The mixture of 0.14 mL of triethylamine and 0.463 g (1.0 mmol) of 5-hydroxy-2-pyrazoline is added, the solution becomes orange. The reaction mixture is refluxed for 3 hours, during this term benzoic anhydride is added on the tip of a spatula once. After the initial pyrazoline disappearance (TLC controlling), reaction mixture is washed with aqueous $NaHCO_3$, then with water, distilled off benzene under reduced pressure and the residue is diluted with ethanol and diethyl ether. 0.41g of light yellow 4-benzoyl-3-(2-nitrophenyl) vinyl)-5-phenyl-1-tosyl-1*H*-pyrazole is filtered after crystallization. The yield constitutes 81%. Mp. = 114–115°C.

IR-spectrum (ν, cm^{-1}): 1648 (C=O), 1517 (NO_2), 1595 (aryl), 1394 (S=O), 1342 (NO_2), 1170 (S=O), 925 (=CH).

NMR-spectrum (ppm, *J* Hz): 2.40 (3H, s, CH_3), 7.17–7.25 (10H, m, aryl, CH=), 7.36 (1H, m, C_6H_5), 7.51–7.58 (7H, m, aryl, CH=), 8.17 (2H, $J = 8.7$, C_6H_4-NO_2).

Conclusion. The determined results testify the high activity of heat stabilizing additives 1-2. The optimum concentration of these substances that cause sufficient strength and elasticity due to aging material is 0.05-0.10 wt.%. It was established that the introduction of investigated additives (1 (1-acetyl-4-methyl-3(5)-(2-(3-nitrophenyl)vinyl)-1*H*-pyrazole) or 2 (4-benzoyl-3-(2-(4-nitrophenyl)vinyl)-5-phenyl-1-tosyl-1*H*-pyrazole)) in LDPE in the amount of 0.05-0.10 wt %. increases such physical-mechanical properties of the samples as tensile strength by 1.2-1.5 times and elongation by 2.3-3.0 times compared to non-stabilized samples. Synthesized substances are more effective than thermostabilizer Tioalkofen MBP used in industry [7].

Saving the strength and elasticity of stabilized samples of LDPE is achieved by suppression of oxidative destruction processes involving molecules of additives 1 and 2, and their contribution to the cross-linking of macromolecules. We should not lose sight of the estimated possible absorption of thermal energy systems by conjugated double bonds which are present in the molecules of additives 1 and 2, thus the reaction centers of polymer macromolecules are inactivated.

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